REMARKS

Claim 2 is pending in this application. By this Amendment, claim 1 is canceled and claim 2 is amended to correct typographical errors. No new matter is added.

The Office Action rejects claims 1 and 2 under 35 U.S.C. § 103(a) as being obvious over Beer (British Patent Specification No. 1,480,807). Claim 1 is canceled, rendering moot the rejection thereof. The rejection is traversed as it may apply to claim 2.

Regarding claim 2, the Office Action indicates that a sintering temperature range and a layer material are the same as those of Beer, and a TiO_2-screening layer is formed between a ruthenium oxide formed while being in contact with a titanium surface and a platinum metal oxide, and thus, a TiO_2-screening layer according to Beer may be used with the same aim as the subject invention. However, it is respectfully submitted that claim 2 of the subject invention would not have been obvious in view of Beer.

However, it is respectfully submitted that the presently claimed invention would not have been obvious in view of Beer.

As for the production of the electrode, prior art, including Beer, suggest a sintering temperature of 400-550°C or 400-650°C (Beer) to oxidize a coating solution, but in the course of practically producing the electrode, the sintering temperature does not exceed 550°C. The reason for this is that, in the case of conducting high temperature sintering at 600°C or higher, since a base metal (or valve metal) is simultaneously oxidized in conjunction with oxidation of a precursor solution, coated on the base metal to form a desired oxide on the base metal, a base metal oxide (TiO_2). That is to say, TiO_2 is solid-diffused to a surface of the desired oxide, thereby occupying a surface of the electrode, resulting in reduced electrode activity, and performances of

the electrode are significantly reduced because surface resistance of the electrode is increased (refer to FIGS. 1 and 2), and the oxide coated on the base metal is easily stripped from the base metal. Unlike the indication in the Office Action, prior art, including Beer, disclose that the sintering of the oxide is conducted at 400-650°C, but do not mention that the performances of the electrode are unexpectedly improved when the sintering is conducted at 600°C or higher (refer to FIGS. 3 and 4).

However, conventional patents or documents describe characteristics of the high temperature sintering, but do not overcome problems, such as increased surface resistance of the electrode, reduced activity of the electrode, and the stripping of the oxide, caused by the diffusion of the base metal oxide (TiO_2) onto an electrode surface because of the oxidation of the base metal when the solution coated on the surface of the base metal is sintered at high temperatures. Thus, it is considered that the rejection of claim 2 is overcome. In other words, the precursor solution ($RuCl_3$, $IrCl_3$ and the like) coated on the surface of the base metal is more sufficiently oxidized during the high temperature sintering than at a conventional sintering temperature, thereby providing improved characteristics to the oxide of the electrode surface.

However, this advantage is completely countervailed by the oxidation of the base metal during the high temperature sintering and the solid diffusion of the base metal into the surface of the oxide (hence, in practice, sintering is usually conducted at temperatures less than 550°C even though Beer's final sintering temperature is within a range of 400-650°C). Moreover, in order to prevent the characteristics of the electrode from being reduced, before the precursor solution ($RuCl_3$, $IrCl_3$ and the like) coated on the surface of the base metal is sintered at high temperatures, a metal oxide layer, such as TiO_2 (it assures a predetermined electric conductivity when it is sintered at 550°C),

SnO_2, IrO_2, or RuO_2, is formed on the surface of the base metal to form another electric conductive oxide layer at 450-550°C, for example, a metal-like oxide layer, on the surface of the base metal, and the solution, which is capable of producing the desired oxide according to a procedure similar to a conventional oxide production process, is coated on the metal oxide layer, dried at 60-70°C, and heat treated at 250-350°C.

This procedure is repeated to increase the number of coated layers, and the resulting structure is finally sintered at 600-700°C to produce the desired oxide layer. In this regard, Beer does not mention the electric conductive oxide layer formed at 450-550°C, that is, the TiO_2 (base metal oxide)-screening layer for preventing the oxidation of the base metal and the solid diffusion of the base metal onto the surface of the desired oxide layer during the final sintering (i.e., metal oxide for preventing the oxidation of base metal and the diffusion of the base metal onto the desired oxide of IrO_2 or RuO_2 during high temperature sintering). As shown in FIG. 5, the additionally applied oxide layer serves to reduce the oxidation of the base metal (Ti) during the high temperature sintering for formation of the final surface oxide, thereby maintaining a high concentration of the desired oxide in the final oxide layer unlike the case of employing no additional oxide layer. Accordingly, it can be seen that oxidation characteristics of organics are improved when the TiO_2 (base metal oxide)-screening layer is employed during high temperature sintering as shown in FIG. 4.

As for present claim 2, although the Examiner asserted that "a TiO_2-screening layer is formed between a ruthenium oxide formed while being in contact with a titanium surface and a platinum metal oxide, and thus, a TiO_2-screening layer according to Beer may be used with the same aim as the subject invention", Beer does not mention the TiO_2-screening layer. The three-stage sintering process described in Beer includes a

drying stage at 80-120°C, a moisture removal and crystallization stage at 175-300°C, and an oxide formation and attachment stage at 400-600°C, which is intended to maintain a multicoated layer to enlarge a layered structure during when the precursor solution ($RuCl_3$ or $IrCl_3$ in solution) is coated in a multilayer coating manner, and to reduce a thermal shock caused by a physicochemical phenomenon during the sintering, and this process is adopted to form the desired oxide layer after the TiO_2-screening layer is formed. When a coating solution ($RuCl_3$ or $IrCl_3$ in solution) is coated in the multilayer coating manner, after the first coating is conducted using the coating solution, water and diluent (the coating solution is an acid or alcohol base solution) are evaporated from the coating solution at 80-120°C and 175-300°C, and metal ions are bonded to oxygen in air to start to form oxide crystals while a Cl component is dissociated.

If the coating solution is additionally applied on the previous layer while this stage is omitted, since the previous layer is not completely dried and set, when the coating solution is additionally painted on the previous layer, the additional coating solution is mixed with the previous insufficiently dried layer, and thus, a laminate having distinct layers cannot be formed. Furthermore, if the coating solution is heated to 400-600°C using a furnace immediately after it is applied on the coated layer, since the base metal and oxide have different thermal expansion coefficients, the coating solution insufficiently adheres to the previous layer and is easily separated from the base metal, and many cracks are formed on the final oxide layer, and thus, the surface becomes unstable. As well, the case of sintering the coating solution directly applied on the Ti base metal is different from the case of forming the TiO_2-screening layer acting as the firm oxide layer between the Ti base metal and the desired oxide layer according to the

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subject invention in view of the diffusion of the oxidized base metal onto the desired oxide layer when the base metal is sintered at high temperatures.

In other words, in the case of employing no TiO$_2$-screening layer, when the solution coated on the surface of the base metal is oxidized by heat, the base metal is heated and oxidized. The base metal oxide is easily diffused from the surface of the base metal to the oxide layer of the electrode surface, and thus, many base metal oxides are present on the electrode surface. However, in the case of employing the TiO$_2$-screening layer, since the firm oxide layer is formed between the base metal and the desired coated layer to be sintered, the base metal oxide is not easily moved to the surface of the desired coated oxide layer. Accordingly, in the case of employing the TiO$_2$-screening layer, when a metal oxide concentration is analyzed according to a depth of the oxide layer as shown in FIG. 4, the base metal component content is low in the final oxide layer. According to the subject invention, the oxide layer, such as TiO$_2$-screening layer, positioned under the final oxide layer, functions to suppress the oxidation of the base metal and the solid diffusion of the base metal to the surface of the oxide layer during the high temperature sintering, and to reduce a concentration gradient of the oxide between the base metal layer and the desired oxide layer, thereby preventing the final oxide layer from being stripped.

Thus, the subject matter of pending claim 2, requiring both sintering at 450°C to 550°C and at 600°C to 700°C, would not have been obvious over Beer, which, at best, only very broadly mentions a single oxide formation and adherence step at 400°C-650°C. Thus, reconsideration and withdrawal of the rejection under 35 U.S.C. § 103(a), as it relates to claim 2, are respectfully requested.

(10/022,357)

Conclusion

In view of the above remarks, Applicants respectfully submit that this application is in condition for allowance. Favorable consideration and prompt allowance of the claims is earnestly solicited. Should the Examiner believe anything further is desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact Applicants' undersigned attorney at the telephone number listed below.

In the event this paper is not considered to be timely filed, Applicants respectfully petition for an appropriate extension of time. The Commissioner is authorized to charge payment for any additional fees which may be required with respect to this paper or credit any overpayment to Counsel's Deposit Account 01-2300, making reference to Attorney Docket No. 101190-00022.

Respectfully submitted,

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Enclosure: Petition for Extension of Time

TECH/259839.1

A study on performance improvement of Ir oxide-coated titanium electrode for organic destruction

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Abstract

The performance improvement of IrO_2 electrode for the oxidative destruction of organics through evaluations of the electrode in terms of material, electrochemical, and destruction organic properties has been carried out by using TGA, XPS, AES, and TOC measurement of 4CP organic destruction at the electrode. A sintering temperature of around 650 °C rather than 400–550 °C suggested in the literature for the Ir oxide electrode enhanced the organic destruction yield because the electrode surface was sufficiently converted to IrO_2 from the $IrCl_3$ of the precursor solution. An additional oxide layer between the IrO_2 layer and the Ti substrate, to prevent a solid diffusion of TiO_2 due to oxidation of the Ti substrate during high-temperature sintering, further improved the organic destruction so that the 4CP destruction yield raised to about four times higher than that by the conventional Ir oxide electrode. The destruction yield of 4CP solution with chloride ion at the improved electrode increased as much as that by an RuO_2 electrode sintered at 430 °C in the same solution. The improved Ir oxide electrode had a long lifetime and good production of active chloride compounds. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Catalytic oxide electrode; DSA; Organic oxidation; RuO_2; IrO_2

1. Introduction

The Dimensionally Stable Anode (DSA) of catalytic oxide electrode, which can generate an active hydroxyl radical and active chlorine species to destroy refractory organic waste into carbon dioxide and water with a relatively low overpotential to oxygen and chlorine evolutions and with a long lifetime, has been widely used in the fields of oxygen, chlorine production, and waste water treatment in the past two decades [1–14]. The most representative DSA are RuO_2/Ti and IrO_2/Ti of a rutile structure. It is known that catalytic activity of RuO_2 is higher than that of IrO_2, whereas the IrO_2 electrode is more stable and has a much longer lifetime than the RuO_2 electrode so that IrO_2 electrode has attracted a greater deal attention than RuO_2 electrode in view of the commercial application of DSA [10,15–18].

However, despite the long lifetime property of the IrO_2 anode, cases of its application to organic waste destruction are very rare, compared with that of RuO_2 anode. Also, organic destruction yield by the IrO_2 electrode has been confirmed in our laboratory to be much lower than those by RuO_2 and SnO_2 electrodes. The DSA electrode is generally evaluated in terms of electrochemical properties such as voltammetric charge capacity representing active surface sites of the oxide electrode, Tafel slope and overpotential for oxygen or chlorine evolution, electrode surface impedance, and so on [4–13]. Even though a DSA has good electrochemical and material properties, the electrode fabricated under those conditions may have a bad result for organic waste destruction. For example, the sintering temperature range of 400–550 °C recommended in the literature [1–10,15–21] for the fabrication of the Ir oxide electrode has been found in our experiments not to be the best temperature for the oxidative destruction of 4-chlorophenol. Therefore, the best fabrication condition of a catalytic oxide electrode for organic waste destruction should be decided after simultaneous evaluations of the

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material, electrochemical, and organic waste destruction properties of the electrode.

In this work, an improvement of Ir oxide electrode performance for organic destruction while keeping a long lifetime of the electrode was investigated by evaluating the several electrode properties mentioned above.

2. Experimental

All reagents for the precursor solutions used in this work were chemical reagent grade and used as received. $RuCl_3$ (Adlich), $TiCl_4$ (Yakuri Chem.) and $IrCl_3$ (Alfa Aesar) were dissolved in 1:1 v/v HCl to prepare the precursor stock solutions of 0.2 M. Demineralized water of 18.2 $M\Omega$ prepared by distilling twice and an ion-exchanger (Mill-Q plus) was used for the preparation of the precursor solution and washing the Ti substrate.

The Ti substrate of the oxide electrode for the measurements of material and electrochemical properties was 99.4% and a plate type of $1 \times 1 \times 0.2$ cm^3 was used. The one for organic destruction was a Madras type of $1 \times 1 \times 0.2$ cm^3 with a mesh of 6×12 mm^2. The Ti substrate was etched in 35% HCl at 61 ± 1 °C for 1 h after decreasing. The etched Ti was thoroughly rinsed with water. The oxide electrodes were prepared by carefully brushing the precursor solution on the etched Ti substrate of plate type, and the Madras type substrate was dipped into the precursor solution. The prepared electrode was dried at 90 °C for 5 min, sintered at 350 °C for 10 min. These steps were repeated to get multiple coating layers and the electrode was finally annealed between 400 and 700 °C for 1 h. The details of the preparation of the oxide electrode was mentioned in our previous papers [13,14,22].

The changes of Ti substrate weight and oxide electrode weight after etching and sintering were measured. For ex-situ analyses, XPS (X-ray photoelectron spectroscopy: VG scientific ESCALB-200R) for the measurement of the composition of compounds near the surface, AES (Auger electron spectroscopy: VG Microlab 300R) for the measurement of composition of compounds along the oxide depth with an etching for cleaning the sample oxide surface by Ar$^+$ sputtering for about 20 min before the measurement, and TGA (Thermogravimetric Analysis: TA instrument SDT 2960) for the measurement of thermal decomposition properties of Ir and Ru chlorides were used. The surface resitivity of the oxide electrode was simply measured by a multi-meter with two probes of a constant distance as an average value of ten times measurements. For in-situ analyses, the electrochemical properties of the oxide electrodes were measured in a three-necked 250 ml volumetric flask with 200 ml of 0.5 M H_2SO_4 at 25 ± 1 °C by using a potentiostat (BAS 100B) with a

reference electrode of a saturated KCl–Ag/AgCl (SSE) and a counter electrode of Pt wire. The lifetime was measured as a time taken for voltage between working and counter electrodes to reach 10 V in 1.0 M H_2SO_4 at 65 °C with a constant current density of 345 mA/cm^2. For the organic destruction test, 4-chlorophenol (4CP) of 30 ppm in pH 7 buffer solution (0.05 M H_3PO_4+0.05 M NaH_2PO_4) was oxidized with Ir oxide electrode as an anode and SUS 316 as a cathode at a current density of 40 mA/cm^2 and in 5 mm distance. The solution was sampled at regular intervals, and then TOC (total organic carbon) in the solution was analyzed by a TOC analyzer (Shimadzu TOC-5000A) where TC (total carbon) and IC (inorganic carbon) in the solution were measured first. The chloride ion and free residual chlorine in the solution during electrolysis were analyzed by the standard DPD methods for Hach DR 2000.

3. Results and discussion

The final sintering temperature for the fabrication of an Ir oxide electrode has been known to have to be between 400 and 550 °C, in other words, not to exceed 600 °C, in the most papers [1–10,15–21]. It is considered that the temperature was decided as the temperature which gave the electrode a low surface resistance and an appropriate electrochemical activity. Fig. 1 shows cyclic voltammograms of Ir oxide electrodes sintered at different temperatures measured between oxygen and hydrogen evolutions at a scan rate of 40 mV/s. As the sintering temperature increases, the measured current is observed to decrease rapidly. It means that the sintering temperature affects the electrode activity greatly. The peaks of the Ir oxide electrode of P1/P2 and P3/P4, which are in agreement with those of published results [11,23], are due to the redox
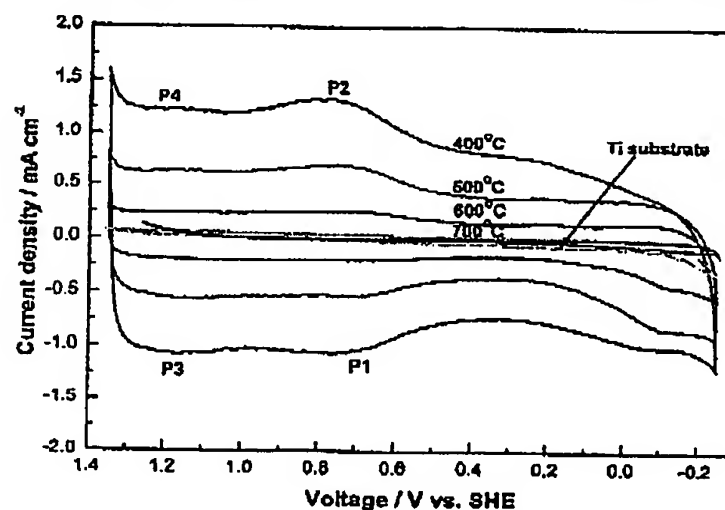

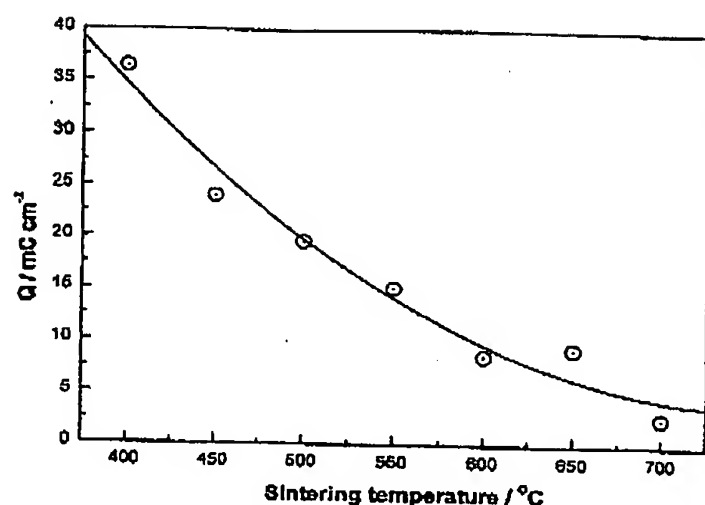Fig. 1. Cyclic voltammogram of Ir oxide electrode in 1.0 M H_2SO_4 with sintering temperature.

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Fig. 2. Voltammetric charge capacity of Ir oxide electrode in 1.0 M H_2SO_4 with sintering temperature.

transitions of electrode surface oxyiridium group species, Ir(III)/Ir(IV) and Ir(IV)/Ir(VI). Fig. 2 shows the voltammetric charge capacity (Q), which is calculated by the integration of a cyclic voltammogram between +0.5 and +1.23 V vs. SHE measured at a scan rate of 40 mV/s and then divided by the scan rate. The voltammetric charge capacity is an important parameter for evaluating the electrochemically active surface area of the oxide electrode. The voltammetric charge capacity of the Ir oxide decreases exponentially with the sintering temperature. Fig. 3 shows the surface resitivity of the Ir oxide electrode with sintering temperature. The surface resitivity keeps under about 1 Ω cm at less than 550 °C, but goes up rapidly after 550 °C so that it comes to about a 1000 Ω cm at 700 °C. The increase of surface resitivity after 550 °C is considered to be attributed to a solid diffusion of the TiO_2 generated from the oxidation of the Ti substrate during high temperature sintering up to electrode surface through the Ir oxide cracks existing
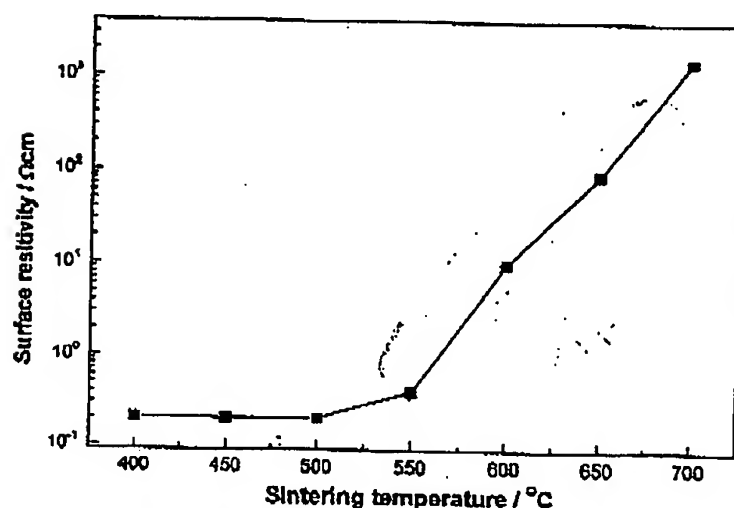
on the Ti substrate. The possibility has been previously suggested elsewhere [13,29]. In order to check this, two wide-scanned XPS spectra near the surfaces of the Ir oxide on the Ti substrate sintered at 400 and 600 °C were measured and are shown in Fig. 4. The Ti $2p_{3/2}$ peak of the Ir oxide sintered at 600 °C becomes much more developed than that at 400 °C, comparing with peaks of Ir 4p, 4d, 4f, because of the solid diffusion of TiO_2 from the Ti substrate to the electrode surface. On the basis of these results of Figs. 1–4, the sintering temperature for the fabrication of an Ir oxide electrode is inferred to be chosen between 400 and 550 °C, taking into consideration of a sintering temperature to give the electrode a suitable electrochemical activity while to keep the surface resistance low.

Fig. 5 shows the removal yields of 4CP at Ir oxide electrodes sintered at different sintering temperatures. The removal yield of 4CP is the best at the electrode sintered at 650 °C, which is about 100 °C higher than the sintering temperature recommended in the literature for Ir oxide electrode. In order to explain the reason, TGA measurements showing the thermal decomposition properties of $IrCl_3$ and $RuCl_3$ used for the precursor solution to be painted on Ti substrate were shown in Fig. 6. The obtained TGA patterns agree with those in literatures [4]. Fig. 6 shows that more than 600 °C is required for $IrCl_3$ to convert sufficiently to Ir oxide. In view of this result, a temperature less than 550 °C is thought to be too low for the preparation of Ir oxide electrode. In Fig. 6, the temperature for $RuCl_3$ to decompose to RuO_2 is about 390 °C. Therefore, the sintering temperature of 400–500 °C suggested for the Ru oxide electrode in the literature [1–20] is considered to be sufficiently high for $RuCl_3$ to convert to Ru oxide. From these results, one of the reasons for the lower 4CP destruction yield below 550 °C than at 650 °C is considered to be due to the insufficient conversion of $IrCl_3$ to Ir oxide. It results in the deficiency of sites on

Fig. 3. Surface resitivity of Ir oxide with sintering temperature.
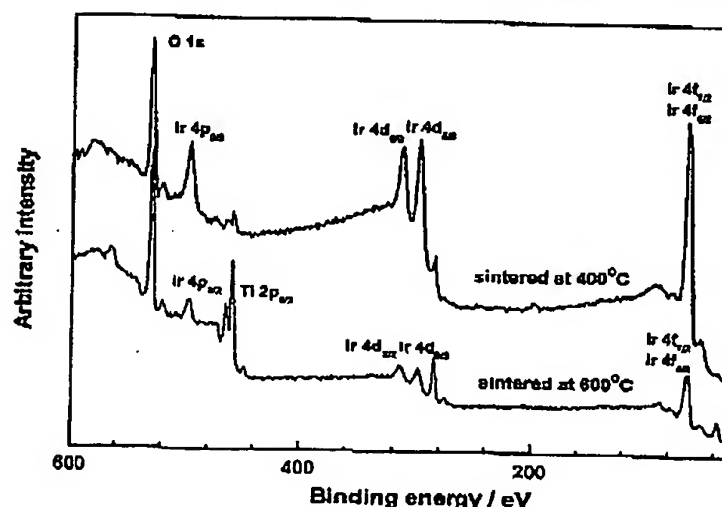

Fig. 4. XPS spectra of Ir oxide sintered at 400 and 600 °C.
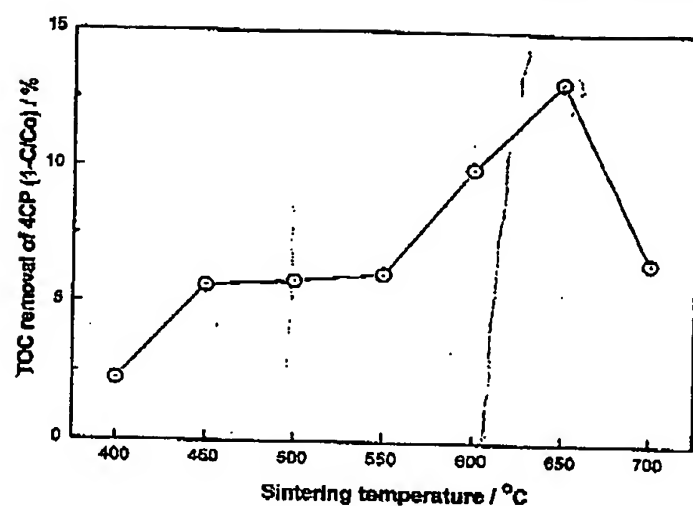
Fig. 5. Removals of 4CP for 2 h by using Ir oxide electrodes of 12 cm² at 40 mA/cm² with sintering temperature of Ir oxide.
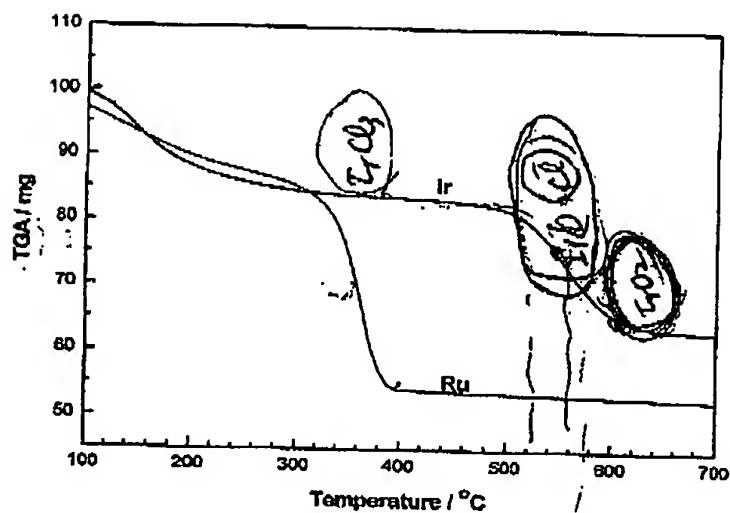

Fig. 7. Removals of 4CP for 2 h by using several Ir oxide electrodes of 12 cm² at 40 mA/cm² in pH 7 solutions with (B) and without (A) chloride ion.

4CP by the Ir oxide electrodes sintered at 450, 550, and 650 °C with and without the TiO₂-screening layer are compared. The 4CP destruction yield at the Ir oxide electrode prepared at 450–550 °C was about 5–6%, and that at 650 °C increased up to about 12%. That at 650 °C with the TiO₂-screening layer comes to 22%, about two times more. In order to confirm the screening effect of the solid diffusion of TiO₂ due to the oxidation of the Ti substrate by the additional valve metal oxide layer, depth profiles of components of Ti, Ir, and O within Ir oxide layer with and without the Ti-screening layer sintered at 650 °C for 1 h were measured by AES, and are shown in Fig. 8. In the case without the Ti-screening layer, the relative composition of Ti is totally higher than that of Ir because much solid-diffusion of TiO₂ due to the oxidation of the Ti substrate occurs. In the case with the TiO₂-screening layer, on the other hand, the results are opposite. This effect was reconfirmed by XPS and the results are shown in Fig. 9. In the case without the TiO₂-screening

Fig. 6. TGA and DTA spectra of IrCl₃ and RuCl₃.

the Ir oxide surface to generate an active hydroxyl radical (OH·) from water [1–9]. The big decrease of the removal yield of 4CP at 700 °C in Fig. 5 is considered to be because the solid diffusion of TiO₂ oxidized from the Ti substrate up to the Ir oxide-coating surface occurs at the high temperature. In that case, some of the active sites of the Ir oxide surface to produce the active hydroxyl radical are covered with the TiO₂ of inert and insulating property.

In this work, in order to overcome the problems which are the decrease of electrode activity and the increase of electrode surface resistance resulting from the solid diffusion of TiO₂ due to the oxidation of the Ti substrate itself at a higher temperature than 600 °C for the purpose of sufficient conversion of IrCl₃ to Ir oxide, another layer of a valve metal oxide, in other words, a TiO₂-screening layer to prevent the solid diffusion of TiO₂ at a high sintering temperature, was added between the Ti substrate and the Ir oxide layer. In Fig. 7(A), the removal yield of
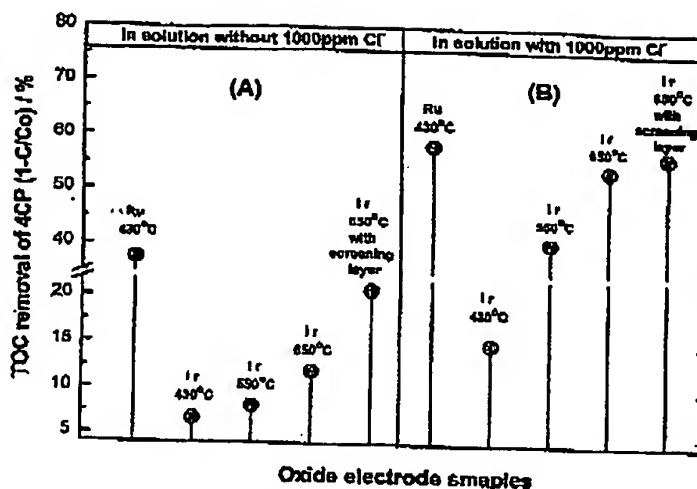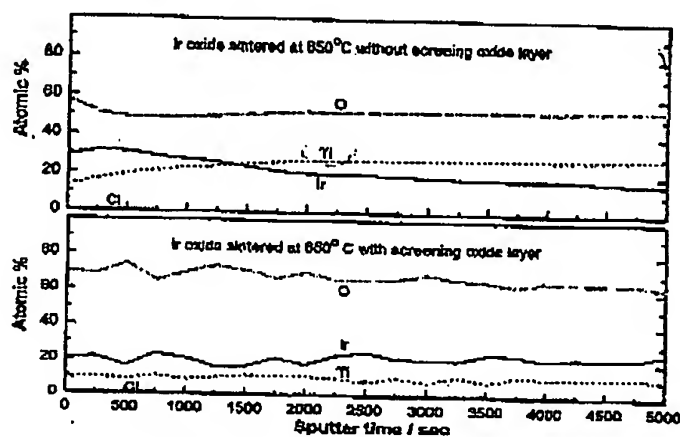

Fig. 8. Concentration depth profiles of Ir, Ti, and O components within Ir oxide layers with and without Ti-screening layer sintered at 650 °C for 1 h.
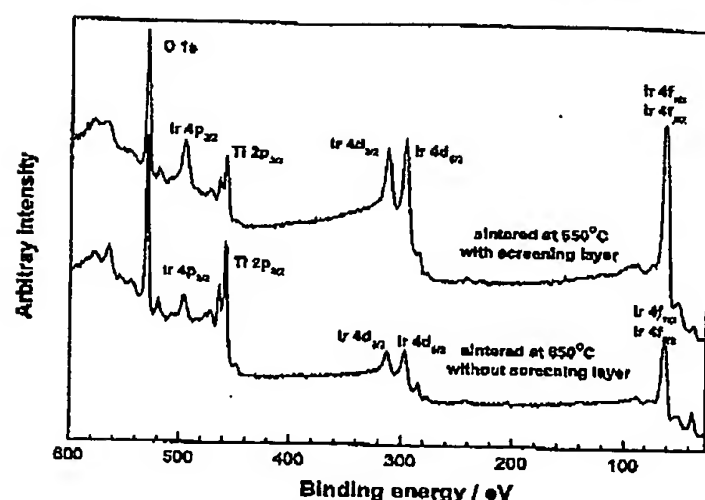
Fig. 9. XPS spectra of Ir oxide layers with and without Ti-screening layer sintered at 650 °C for 1 h.

Fig. 10. Removals of 4CP for 2 h using several Ir oxide electrodes of 12 cm² at 40 mA/cm² in pH 7 solutions.

layer, the Ti peak becomes relatively better developed as compared with that of Ir. However, for the case of the Ir oxide electrode with the TiO₂-screening layer, Ti peak goes down to be relatively lower than the Ir peaks. The surface resitivity at 650 °C without the TiO₂-screening layer is ~ 100 Ω cm, as seen in Fig. 3. However, the value in the case with the TiO₂-screening layer was experimentally measured to become less than 10 Ω cm. This means that the amount of TiO₂ generated at a high temperature on electrode surface has a great effect on the surface resistance. All these results provide a convincing argument that increase of the sintering temperature for the Ir oxide electrode up to 650 °C so as to convert sufficiently $IrCl_3$–IrO_2 while controlling the solid-diffuion of TiO₂ due to Ti substrate oxidation by an additional TiO₂-screening layer can effectively enhance oxidative organic destruction yield.

Papers [10,15,24,25] relating to the DSA of IrO_2 or RuO_2 show an attempt to improve the electrochemical properties by a TiO_2–IrO_2 or TiO_2–RuO_2 mixture electrode sintered at 450–550 °C after adding $TiCl_4$ into the precursor solution of $IrCl_3$ or $RuCl_3$. Therefore, it could be thought that the high sintering temperature more than 600 °C used in this work makes naturally TiO₂ itself due to the oxidation of Ti substrate within the IrO_2 or RuO_2, thus the existence of TiO₂ results in the increase of 4CP destruction yield. Accordingly, only an artificially addition of TiO₂ in an IrO_2 or RuO_2 electrode prepared at a low temperature less than 550 °C not to generate the oxidation of the Ti substrate may increase the organic destruction yield. To confirm it, the removal yields of 4CP at IrO_2–TiO_2 mixed electrodes sintered at 500 °C with precursor solutions of ratios of $IrCl_3$–$TiCl_4$ of 5:5 and 3:7 were compared with those at an IrO_2 electrode prepared at 650 °C with and without TiO₂-screening layer, and shown in Fig. 10. It shows that the removal yields of 4CP at IrO_2–TiO_2
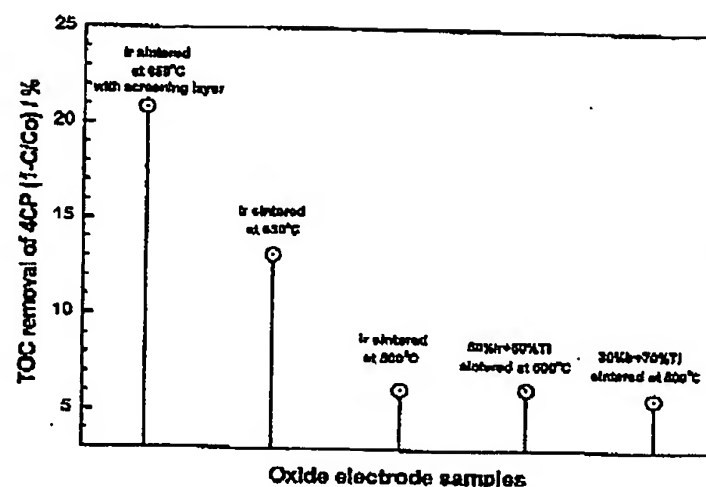
mixed electrodes sintered at 500 °C are almost the same to that at IrO_2 electrode prepared at 500 °C. It means that the existence of TiO₂ itself does not affect the organic destruction yield, but the sintering temperature does.

In Fig. 7(B), removal yields of 4CP in a solution of pH 7 with the chloride ion of 1,000 ppm by using several IrO_2 electrodes and an RuO_2 electrode sintered at 430 °C were compared with those at the same electrodes in the solution without the chloride ion of Fig. 7(A). In the case of the solution without the chloride ion, the removal yield of 4CP at RuO_2 electrode is about 37.5%, but in the case with the chloride ion, it increases to 58%. The removal yield of 4CP by using the improved Ir oxide electrode with the TiO₂-screening layer in the solution without chloride ion is 22%, however, the value in the case of the solution with the chloride ion goes up to 57% as much as that by the RuO_2 electrode. An Ir oxide electrode sintered at less than 550 °C cannot destruct 4CP as much as that at the Ru oxide electrode even in a chloride ion solution. The chloride ion is known to change into active chloride compounds such as hypochlorite ion, hypochlorite acid, chlorate ion at the catalytic oxide electrode that are effective in attacking organics like the active hydroxyl radical [26–28]. The generation mechanism at the electrode is explained, as follows.

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + H_2O \rightleftharpoons HClO + Cl^- + H^+ \tag{2}$$

$$HClO \rightleftharpoons H^+ + ClO^- \tag{3}$$

$$6ClO^- + 3H_2O$$
$$\rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2O_2 + 6e^- \tag{4}$$

$$ClO_3^- + H_2O \rightarrow 2ClO_4^- + 2H^+ + 2e^- \tag{5}$$

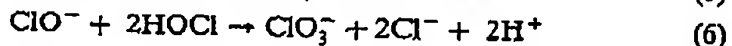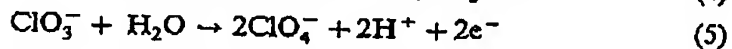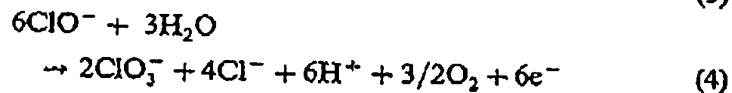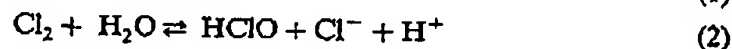$$ClO^- + 2HOCl \rightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{6}$$

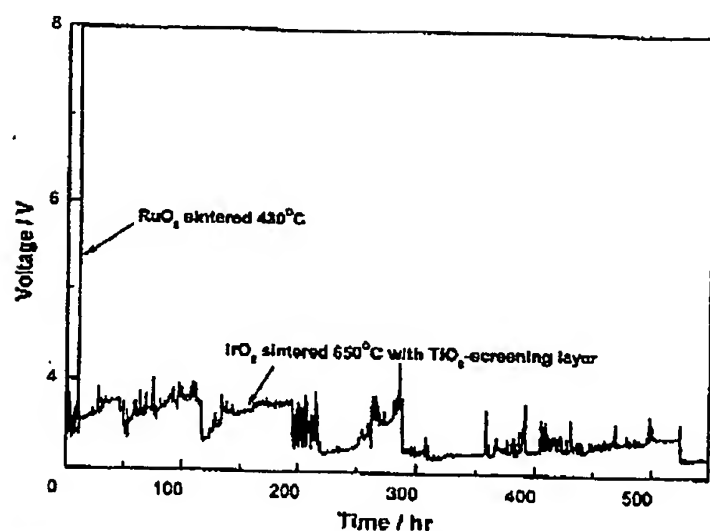Fig. 11 shows an accelerated lifetime test of a Ru oxide electrode prepared at 430 °C and an Ir oxide

Fig. 11. Lifetime of RuO$_2$ and IrO$_2$ electrodes in 1.0 M H$_2$SO$_4$ at 65 °C at a current density of 345 mA/cm^2.

Fig. 12. Changes of chloride ion and free residual chlorine generated at several oxide electrodes of 12 cm^2 at 40 mA/cm^2 in solutions with time.

electrode prepared at 650 °C with the Ti-screening layer that were carried out in 1.0 M H$_2$SO$_4$ at 65 °C at a current density of 345 mA/cm^2. Both electrodes had four Ir or Ru oxide layers by dipping them in 0.2 M precursor solutions and sintering repeatedly. The lifetime of the Ru electrode was about 10.6 h at which time bare Ti substrate appeared on the electrode and the measured voltage between the cathode and anode rose suddenly up to more than 10 V. In the case of the Ir oxide electrode, the end of lifetime was not observed in the experiment period of about 550 h. These results mean that the improved Ir oxide electrode for organic destruction is as stable as the conventional Ir oxide electrode. The lifetime of the Ir oxide electrode is guessed to be able to have more than 2000 h/mg$_{IrO_2}$ on the basis of our previous experiments on Ir oxide electrodes. The fluctuation of the measured current in Fig. 11 was due to vigorous gas evolution and periodical changes of the electrolyte solution and damaged cathode.

In order to estimate amounts of active chloride compounds generated from chloride ion in solution at the Ir and Ru oxide electrodes, the changes of the chloride ion and free residual chlorine compounds (Cl$_{2,Aqeous}$, HClO, ClO$^-$) during electrolyses by using the electrodes of 12 cm^2 at 40 mA/cm^2 were measured and shown in Fig. 12. The decrease of chloride ion concentration at the improved Ir oxide electrode sintered at 650 °C with the TiO$_2$-screening layer is larger than those at the Ru oxide electrode sintered at 430 °C and at the Ir oxide electrode sintered at 500 °C. The amount of chloride ion, which disappeared in the solution, is considered to change into Cl$_{2,Aqeous}$, Cl$_{2,Gas}$, HClO, ClO$^-$, etc. through Eqs. (1)–(6). The amounts of free residual chlorine compounds by all the electrodes are similar. From all these results from Fig. 5 to Fig. 12,
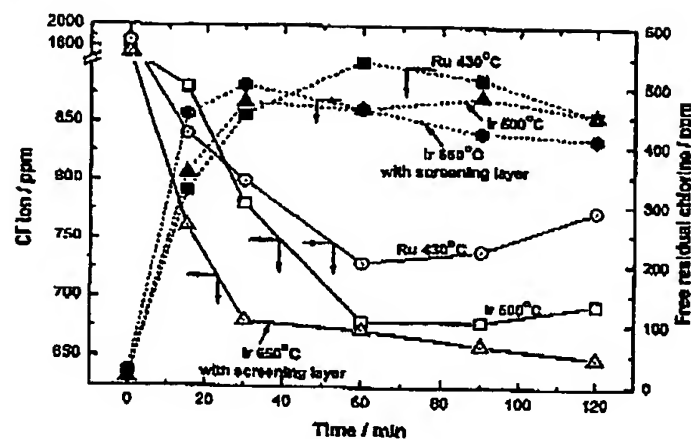
the Ir oxide electrode sintered at 650 °C with the TiO$_2$-screening layer can be said to show a big improvement for organic destruction while keeping a long lifetime and an effective generation of active chloride compounds or active hydroxyl radical, compared with the Ir oxide electrode prepared at 450–550 °C.

4. Conclusions

An Ir oxide electrode sintered at around 650°C rather than 400–550 °C suggested in the literature enhanced organic destruction because the electrode surface was sufficiently converted to IrO$_2$ from the IrCl$_3$ of the precursor solution. The additional TiO$_2$-screening layer between the IrO$_2$ layer and the Ti substrate, preventing the solid diffusion of TiO$_2$ oxidized from the Ti substrate during high-temperature sintering, further enhanced the organic destruction. The 4CP destruction yield on such improved electrode raised to about four times higher than that by the conventional Ir oxide electrode. The removal yield of the 4CP in the solution with the chloride ion at the improved electrode increased as much as that by the RuO$_2$ electrode sintered at 430 °C in the same solution. The improved Ir oxide electrode had a long lifetime and a good production of active chloride compounds.

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Material and Organic Destruction Characteristics of High Temperature-Sintered RuO₂ and IrO₂ Electrodes

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For Ru and Ir oxide electrodes sintered at different temperatures, in this work, surface resistivity, X-ray photoelectron spectroscopy, electrode lifetime, voltammetric charge capacity, and total organic carbon of 4-chlorophenol (4CP) decomposition at the electrodes were measured, and then intermediates during the electrolysis were identified by gas chromatography-mass spectroscopy to predict the destruction path of 4CP at the electrodes. A sintering temperature of around 650°C, rather than 400-550°C suggested in the literature for the fabrication of Ru and Ir oxide electrode, showed the highest organic destruction yield. The sintering temperature strongly affected the electrode lifetime as well. During the high temperature sintering, increase of the sintering time caused the oxidation of the Ti substrate to result in the increase of oxide weight of the electrode and the solid diffusion of the generated TiO₂ to the electrode surface, which decreased the electrode activity so that the organic destruction yield went down slowly. The destruction path of 4CP at a high temperature-sintered electrode was suggested to be different from that at a low temperature-sintered one. The Ru oxide electrode sintered at 450°C generated several complicated aliphatic intermediates. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1515280] All rights reserved.

Catalytic oxide electrodes, called dimensionally stable anodes (DSAs), can generate active hydroxyl radicals and active chloride species to destroy refractory organic waste into carbon dioxide and water with a relatively low overpotential for oxygen and chlorine evolution and with a long lifetime.[1-14] Such electrodes have been widely used in the fields of oxygen and chlorine production, as well as wastewater treatment in the past two decades. The most representative DSAs are RuO₂/Ti and IrO₂/Ti of a rutile structure. It is known that the catalytic activity of RuO₂ is higher than that of IrO₂, whereas the IrO₂ electrode is more stable and has a much longer lifetime than the RuO₂ electrode so that the IrO₂ electrode has attracted greater attention than the RuO₂ electrode for the commercial application of DSA.[10,15-18]

The sintering temperature recommended in the literature[1,10,15-23] for the Ru and Ir oxide electrodes is 400-550°C, not to exceed 600°C, taking into consideration the electrochemical and material properties of the electrodes. The fabricated DSA electrode is generally evaluated in terms of electrochemical properties such as voltammetric charge capacity representing active surface sites of the oxide electrode, Tafel slope and overpotential for oxygen or chlorine evolution, electrode surface impedance, and so on.[4-13] Even though a DSA has good electrochemical and material properties, the electrode may not be effective for organic waste treatment. In our previous work,[24,25] for example, an IrO₂ electrode sintered at 400-550°C, showing the best electrochemical and material properties, did not destroy 4-chlorophenol (4CP) more effectively than those sintered at 600-650°C. This means that the usual sintering temperature for catalytic electrodes mentioned in the literature may not be the best temperature for preparation of electrodes for the oxidative destruction of 4CP. Therefore, the best fabrication condition of a catalytic oxide electrode for organic waste destruction should be chosen after simultaneous evaluation of the material, and of the electrochemical and organic waste destruction properties of the electrode.

The sintering temperature is the most important variable among several variables affecting fabricated catalytic oxide electrodes. In this work, therefore, the material, electrochemical, and organic destruction properties of Ru and Ir oxide electrodes were measured with different sintering temperatures and then the decomposition mechanisms of 4CP to carbon dioxide at Ru and Ir oxide electrodes sintered at low and high temperatures were evaluated and compared.

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Experimental

All reagents for the precursor solutions used in this work were chemical reagent grade and used as received. RuCl₃ (Aldrich) and IrCl₃ (Alfa Aesar) were dissolved in 1:1 v/v HCl to prepare precursor stock solutions of 0.2 M. Demineralized water of 18.2 MΩ prepared by distilling twice, and an ion-exchanger (Milli-Q plus) were used for the preparation of the precursor solution and washing the Ti substrate.

The Ti substrate of the oxide electrode for the measurements of material and electrochemical properties was 99.4% and a plate type of 1 × 1 × 0.2 cm dimensions was used. The one for organic destruction was a Madras type of 1 × 1 × 0.2 cm with a mesh of 6 × 12 mm. The Ti substrate was etched in 35% HCl at 61 ±1°C for 1 h after degreasing. The oxide electrodes were prepared by carefully brushing the precursor solution onto the etched Ti substrate of the plate type, and the Madras-type substrate was dipped into the precursor solution. The prepared electrode was dried at 90°C for 5 min and sintered at 350°C for 10 min. These steps were repeated to get multiple coating layers and the electrode was finally annealed between 400 and 700°C for 1 h. The net oxide weight on the Ti substrate used in this work are about 0.371 mg/cm² for Ir oxide and about 0.21 mg/cm² for Ru oxide after final sintering below 550°C from which the Ti substrate itself is oxidized to cause the increase of weight of the net oxide on the Ti substrate. The details of the preparation of the oxide electrode are mentioned in our previous papers.[13,14,22-25]

The changes in Ti substrate weight and oxide electrode weight after etching and sintering were measured. For *ex situ* analyses, X-ray photoelectron spectroscopy (XPS, VG scientific ESCALAB-200R) was used for the measurement of the composition of compounds near the surface. The surface resistivity of the oxide electrode was simply measured by a multimeter with two probes of a constant distance as an average value of ten measurements. For *in situ* analyses, the electrochemical properties of the oxide electrodes were measured in a three-necked 250 mL volumetric flask with 200 mL of 0.5 M H₂SO₄ at 25 ± 1°C by using a potentiostat (BAS 100B) with a reference electrode of a saturated KCl-Ag/AgCl saturated sulfate electrode (SSE), and a counter electrode of Pt wire. The accelerated lifetime was measured as the time taken for the voltage between working and counter electrodes to reach 10 V in 1.0 M H₂SO₄ at 65°C with a constant current density of 1,000 mA/cm². For the organic destruction test, 4CP of 30 ppm in pH 7 buffer solution (0.05 M H₃PO₄ + 0.05 M NaH₂PO₄) was oxidized with a Ru or Ir oxide electrode as an anode and SUS 316 as a cathode at a
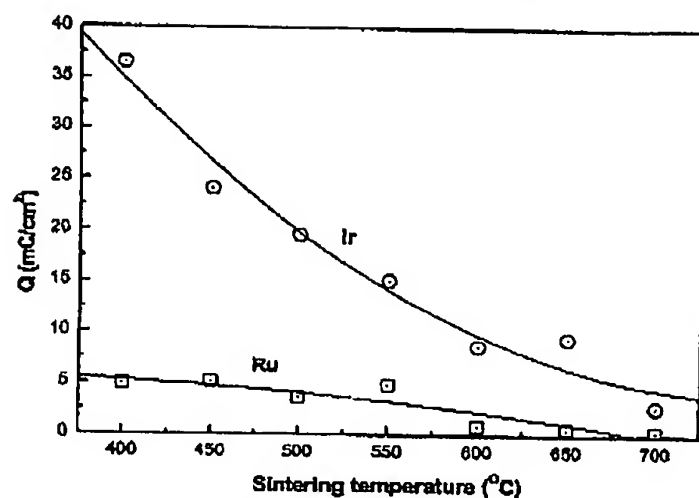
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Figure 1. Voltammetric charge capacities of Ir and Ru oxide electrodes in 1.0 M H_2SO_4 with sintering temperature.

Figure 2. Surface resistivities of Ir and Ru oxide electrodes with sintering temperature.

current density of 40 mA/cm^2 and with 5 mm separation. The solution was sampled at regular intervals; the total organic carbon (TOC) in the solution was analyzed by a TOC analyzer (Shimadzu TOC-5000A) where TC (total carbon) and IC (inorganic carbon) in the solution were measured first. The intermediate species generated in the solution during the electrolysis were detected and evaluated by gas chromatography (GC, Hewlett Packard 6890)-mass spectroscopy (Hewlett Packard 5973N MSD).

Results and Discussion

The best final sintering temperature for the fabrication of Ir and Ru oxide electrodes has been reported to be between 400 and 550°C, in other words, not to exceed 600°C, in most papers.[1-10,13-21] It is considered that the temperature which gave the electrode a low surface resistance and an appropriate electrochemical activity was selected.

Figure 1 shows the voltammetric charge capacities (Q) of Ir and Ru oxide electrodes, which are calculated by the integration of a cyclic voltammogram between +0.5 and +1.23 V vs. saturated hydrogen electrode (SHE) measured at a scan rate of 40 mV/s and then divided by the scan rate. The voltammetric charge capacity is an important parameter for evaluating the electrochemically active surface area of the oxide electrode. The voltammetric charge capacity of the Ir oxide electrode is much higher than that of Ru oxide when both electrodes are prepared with precursor solutions of the same concentration. The values of the Ir and Ru oxide electrodes decrease with the sintering temperature. However the decrease for the Ir oxide electrode is more distinct and rapid. Table I provides the real Brunauer-Emmett-Teller (BET) values of Ru and Ir oxide electrodes sintered at 450 and 600°C. The relative values of BET of Ru and Ir oxide electrodes sintered at 450 and 600°C are similar to those of the voltammetric charge capacities in Fig. 1 so that it is considered that the electrochemically active sites of the electrode have a close relationship to the actual geometric surface area of the electrode.

Figure 2 shows the surface resitivities of the Ir and Ru oxide electrodes with sintering temperature. The surface resitivity remains
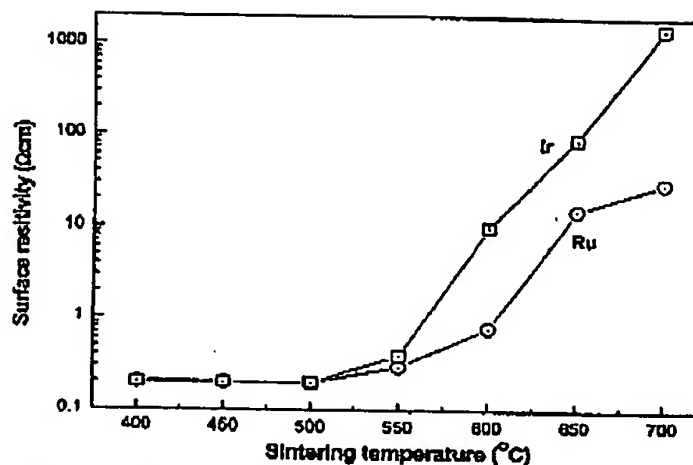
under about 1 Ω cm at less than 550°C, but goes up rapidly above 550°C so that the surface resistivity of Ir oxide increases to ~1,000 Ω cm at 700°C. The rapid increase of surface resitivity above 550°C is attributed to solid diffusion of TiO_2, generated from the oxidation of the Ti substrate during high temperature sintering, up to the electrode surface through the Ir or Ru oxide cracks existing on the Ti substrate. This interpretation has been suggested elsewhere[13,26] and confirmed by XPS analysis in our previous work.[23-25] In the case of a bare Ti substrate without Ir or Ru oxide coating, the surface resistivity of less than 1 Ω cm below 500°C went up to a few times 10^5 Ω cm at more than 600°C.[13] However, in the case of a Ti substrate on which other metal-like oxide materials such as Ir or Ru oxide were coated, the surface resistivity did not increase very much, because the Ir or Ru oxide layer on the Ti substrate prevents oxidation of the Ti substrate and because the oxide layer on the Ti substrate suppresses the solid diffusion of any TiO_2 formed by oxidation of the Ti substrate during high temperature sintering. The oxidation of the Ti substrate above 550°C results in an increase of oxide weight of electrode; the results are shown in Fig. 3. The ratio of weights of Ir and Ru oxides on the electrodes below 550°C, which were coated with Ir and Ru precursor solutions of the same concentration, is
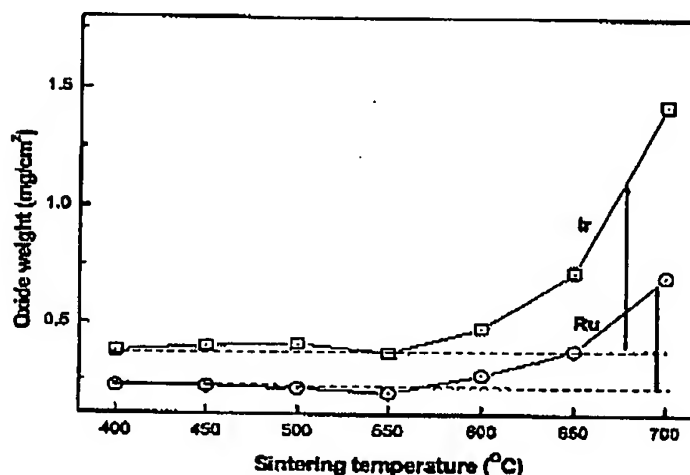

Figure 3. Net weight changes of Ir and Ru oxide electrodes sintered for 1 h after coating Ti substrate with 0.2 M precursor solution with sintering temperature.

Table I. BET of IrO_2 and RuO_2 sintered at 450 and 600°C.

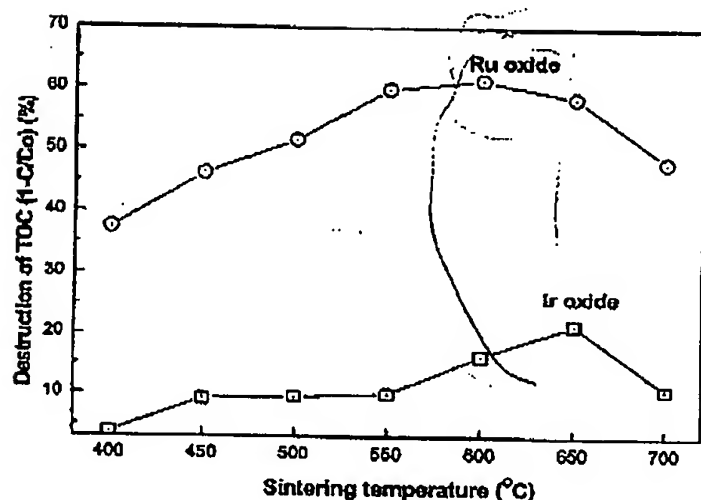| Oxide electrode	IrO_2 at 450°C	IrO_2 at 600°C	$Ru\,O_2$ at 450°C	$Ru\,O_2$ at 600°C
BET (m^2/g_{oxide})	340	128	151	9

Figure 4. Destruction yields of TOC for 2 h by using Ir and Ru oxide electrodes of 12 cm^2 at 40 mA/cm^2 with sintering temperature.

Figure 6. XPS spectra of Ir and Ru oxide layers sintered at 650°C for 1 and 4 h.

about 1.72 which is close to the atomic weight ratio of IrO$_2$ to RuO$_2$ of 1.67. The results of Fig. 1 to 3 mean that the sintering temperature range between 400 and 550°C is suitable in view of the fabrication of Ir and Ru oxide electrodes with good electrochemical activity while keeping the surface resistance low.

Figure 4 shows the destruction yields of TOC for treatment of 4CP by Ir and Ru oxide electrodes sintered at different sintering temperatures. The removal yield of TOC from 4CP is the best at electrodes sintered at about 650°C, which is about 100 to 200°C higher than the conventional sintering temperature in the literature for Ir and Ru oxide electrodes. In order to explain the reason, the results of thermogravimetric analysis (TGA) showing the thermal decomposition properties of IrCl$_3$ and RuCl$_3$, which were used as the precursor solution to be painted on the Ti substrate, were examined first. The TGA results have been reported in the literature and in our previous work.[4,25] The result shows that more than 600°C is required for IrCl$_3$ to be converted to Ir oxide. In view of this result, a temperature less than 550°C is thought to be too low for the preparation of an Ir oxide electrode. On the other hand, the tempera-
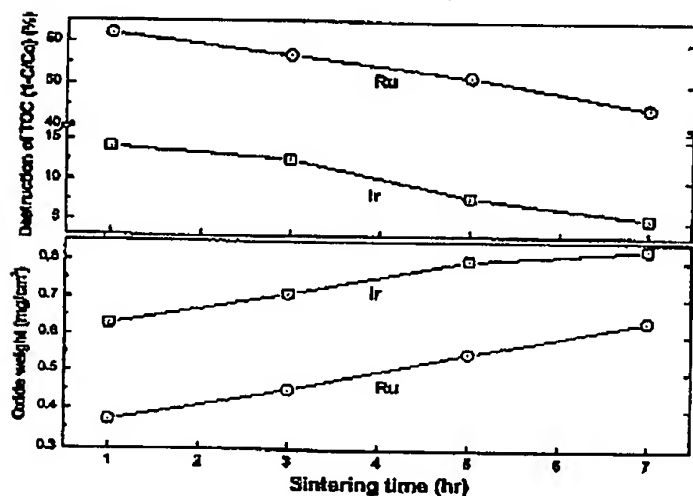
ture for RuCl$_3$ to decompose to RuO$_2$ is about 390°C. Therefore, the sintering temperature of 400-500°C suggested for the Ru oxide electrode in the literature[1-20] is considered to be sufficiently high for RuCl$_3$ to be converted to Ru oxide. From these results, in the case of the Ir oxide electrode, one of the reasons for the lower 4CP destruction yield below 550°C compared to 650°C is considered to be insufficient conversion of IrCl$_3$ to Ir oxide. This results in a deficiency of sites on the Ir oxide surface to generate active hydroxyl radical (OH$^-$) from water.[1-9] However, in the case of Ru oxide, the degree of conversion of RuCl$_3$ to Ru oxide cannot be used to explain the better organic destruction yield at a Ru oxide electrode sintered at temperatures over 600°C, because the conventional sintering temperature of 400-500°C is sufficient for RuCl$_3$ to be converted to an appropriate Ru oxide structure. Therefore, another reason for the better organic destruction at Ru oxide electrodes is necessary. This is discussed again after Fig. 8. The big decrease of the removal yield of 4CP at 700°C in Fig. 4 is considered to be caused by solid dif-

Figure 5. Destruction yields of TOC by the oxide electrodes of 12 cm^2 at 40 mA/cm^2 and oxide weights of Ir and Ru oxide electrodes sintered at 650°C with a change of sintering time.
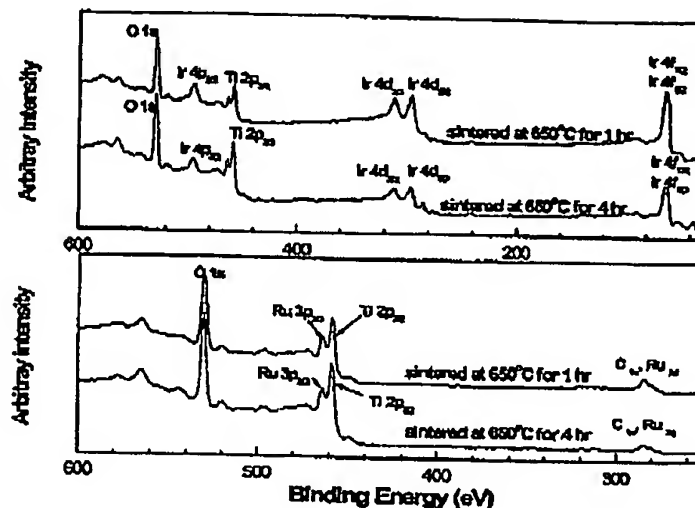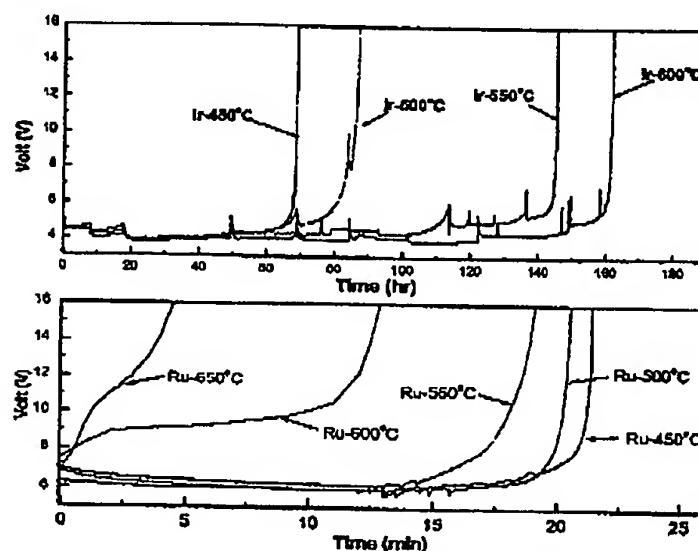

Figure 7. Lifetimes of Ir and Ru oxide electrodes with sintering temperature in 1.0 M H$_2$SO$_4$ at 65°C at 1,000 mA/cm^2.
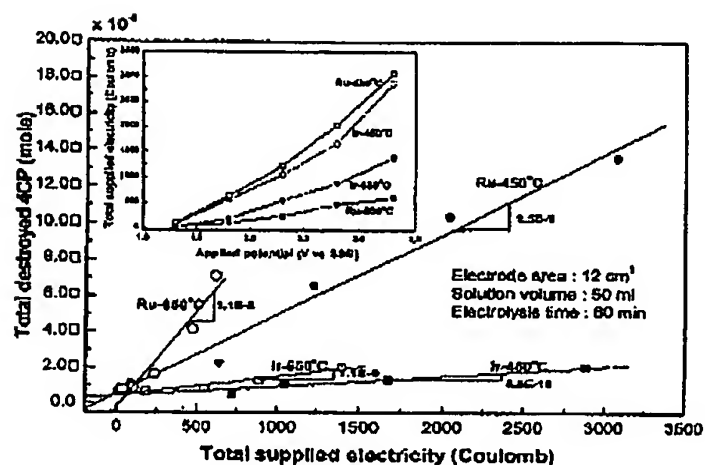
Figure 8. Total amount of 4CP destroyed by using Ir and Ru oxide electrodes of 12 cm² sintered at 450 and 650°C at 40 mA/cm² for 1 h.

fusion of TiO_2, formed by oxidation of the Ti substrate, up to the Ir or Ru oxide-coating surface. In that case, some of the active sites to produce the active hydroxyl radical at the oxide surface are covered with TiO_2 with an inert and insulating property.[13,23-26] From the results of Fig. 1-4, it is considered that the best fabrication conditions for catalytic oxide electrodes for the destruction of organics should be decided after taking into account all the factors of the material, electrochemical, and organic waste destruction properties.

Although a sintering temperature between 600 and 650°C gives the oxide electrode better properties for organic destruction, as mentioned above, sintering the electrode for a long time could allow solid diffusion of TiO_2 to the electrode surface due to the oxidation of Ti substrate itself, which would result in increases of oxide weight on the electrode and inactivation of the electrode surface. To confirm this, the changes of oxide weight on the electrode and destruction yield of TOC were measured as a function of sintering time at 650°C, and the changes of the XPS spectra at Ir and Ru oxide electrodes sintered at 650°C for 1 and 4 h were measured together. They are shown in Fig. 5 and 6, respectively. As shown in Fig. 5, the oxide weight increases almost linearly with an increase of the sintering time due to the continuous oxidation of the Ti substrate, which causes the activity of the electrode to be lowered so that the
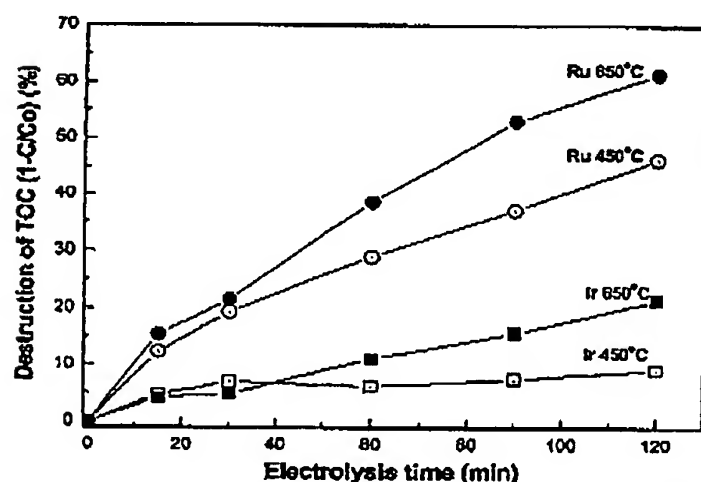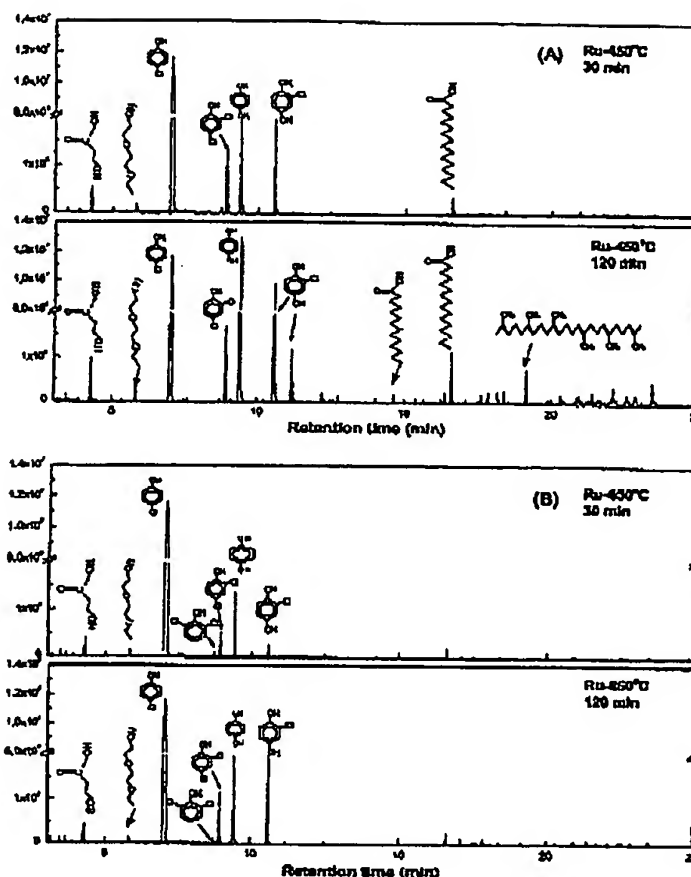

Figure 10. TIC after electrolysis of 4CP solutions for 30 and 120 min at Ru oxide electrodes sintered at (A) 450°C and (B) 650°C.

destruction yield of 4CP becomes lower. In Fig. 6, the Ti $2p_{3/2}$ peaks of Ir and Ru oxide electrodes sintered at 650°C for 4 h become relatively more developed than those at 650°C for 1 h, compared with Ir peaks of 4p, 4d, 4f, and Ru peaks of $3p_{3/2}$ and 3d, respectively, because of the solid diffusion of TiO_2 from the Ti substrate to the electrode surface. These results mean that controlling the sintering time at a high temperature is very important.

Figure 7 shows accelerated lifetime tests[27,28] of Ir and Ru oxide electrodes prepared at 450-650°C, which were carried out in 1.0 M H_2SO_4 at 65°C at a current density of 1,000 mA/cm². All the electrodes had four Ir or Ru oxide layers that were formed by dipping them in 0.2 M precursor solutions and sintering repeatedly. Generally, the lifetime of the Ir oxide electrodes is much longer than that of Ru oxide electrodes, however surprisingly, the lifetime of the Ir oxide electrode increases with the sintering temperature, whereas that of the Ru oxide electrode decreases with the sintering temperature. This lifetime property of the electrodes is very important with respect to commercial application of the electrodes. The fluctuation of the measured current in Fig. 7 was due to vigorous gas evolution and periodic changes of the electrolyte solution and damaged cathode.

Figure 8 shows the changes of the amounts of decomposed 4CP by electricity supplied for 1 h at several voltages where oxygen evolution occurs, at Ir and Ru oxide electrodes sintered at 450 to 650°C, respectively. An inset showing the relationship between supplied electricity and applied voltage is included in Fig. 8 as well. At the same voltage, the supplied electricity at the electrode sintered at 450°C is higher than that at 650°C. That is considered to have something to do with the electrode surface resistivity in Fig. 2. The
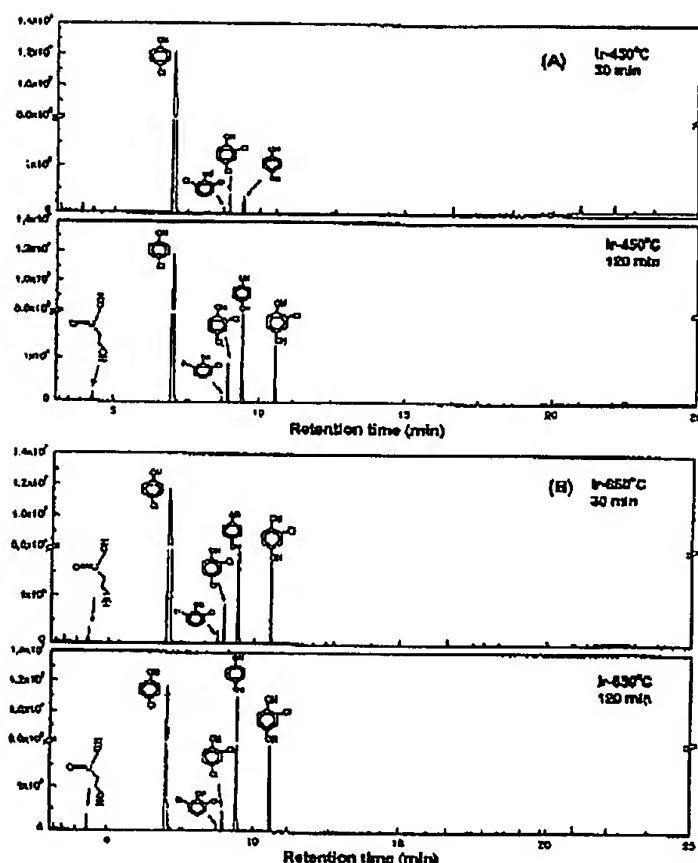

Figure 9. Destruction yields of TOC by using Ir and Ru oxide electrodes of 12 cm² sintered at 450 and 650°C at 40 mA/cm² with electrolysis time.

Figure 11. TIC after electrolysis of 4CP solutions for 30 and 120 min at Ir oxide electrodes sintered at (A) 450°C and (B) 650°C.

amount of destroyed 4CP is linear to the total supplied electricity. This means that the active hydroxyl radical (OH⁻) to be able to destroy organics is produced linearly with the supplied electricity. If the electrode property prepared at a certain temperature is the same as that prepared at a different temperature, it makes sense that both electrodes should have the same organic destruction yields at the same amount of supplied electricity. However, a noteworthy thing in Fig. 8 is that the 4CP destruction yield by the Ru or Ir oxide electrode sintered at 650°C is higher than that by the Ru or Ir oxide electrode sintered at 450°C at the same amount of electricity. This

result means that the electrode prepared at 650°C has a different material structure to generate the hydroxyl radical more effectively, compared with that sintered at 450°C, although the electrode prepared at 650°C has less electrochemical activity as shown in Fig. 1.

Figure 9 shows the variation of the destruction yield of TOC at Ir and Ru oxide electrodes sintered at 450-650°C with electrolysis time. Figures 10 and 11 show total ion chromatograms (TIC) measured by GC-mass spectroscopy, which show intermediates generated from 4CP at 30 and 120 min of electrolysis at Ir and Ru oxide electrodes sintered at 450-650°C. Table II summarizes all the intermediate compounds identified by GC-mass spectroscopy with their retention times. The destruction yield of 4CP increases linearly with the electrolysis time, and the destruction rate by the electrode sintered at 650°C is higher than that by the electrode sintered at 450°C, as mentioned above. In the cases of both Ru oxide electrodes sintered at 450 to 650°C, aromatic intermediates such as hydroquinone, 1,4-dihydroxy-2-chlorobenzene, and dichlorophenols appear at 30 and 120 min of electrolysis, and their amounts at 120 min are much more than those at 30 min. Also, low molecular weight aliphatic compounds such as 2-hydroxypropanoic acid and 1-(2-ethoxyethoxy)-2-hydroxyethane are found in all the cases. However, in the case of the Ru oxide electrode sintered at 450°C, very large aliphatic compounds such as tetradecanoic acid, hexadecanoic acid, etc., which are not found at the Ru oxide electrode sintered at 650°C, are found with time. And, many unidentified peaks at the electrode sintered at 450°C appearing at 120 min of electrolysis are considered to be due to more complicated compounds. Those compounds are considered to be synthesized through polymerization reactions of the intermediate compounds. As the TOC decreases with the electrolysis time at the Ru oxide electrode sintered at 450°C, it is considered that both paths of the conversion of 4CP and its intermediates to CO_2 and the polymerization to complicated compounds of higher oxidation states occur at the same time as the electrode. On the other hand, at the Ru oxide electrode sintered at 650°C, it is considered that the conversion of 4CP to aromatic intermediates like hydroquinone and the combustion of them to CO_2 occur mainly without the polymerization reaction, because the complicated compounds are not found at 120 min of electrolysis. Accordingly, from these results, it is naturally inferred that the organic destruction rate at the Ru oxide electrode sintered at 650°C is faster than that at the Ru oxide electrode sintered at 450°C with the same amount of electricity, as shown in Fig. 9, because the hydroxyl radical generated at the electrode sintered at 650°C is used only for the combustion of the aromatic intermediates to CO_2 without the consumption of the hydroxyl radical for synthesis of the higher oxidation state compounds. In the case of the Ir oxide electrode, the compounds found at the electrode sintered at 650°C are the same as those generated at the Ru oxide electrode sintered at 650°C. However, at the Ir oxide electrode sintered at 450°C, the amounts of generated hydroquinone,

Table II. Intermediates generated during electrolysis of 4CP by RuO_2 and IrO_2 electrodes.

| Compound	Retention time (min)	Molecular formula
2-Hydroxy propanoic acid	4.28	$C_3H_6O_3$
1-(2-Ethoxyethoxy)-2-hydroxyethane	5.81	$C_6H_{14}O_3$
4-Chlorophenol	7.03	C_6H_5ClO
2,6-Dichlorophenol	8.73	$C_6H_4Cl_2O$
2,4-Dichlorophenol	8.95	$C_6H_4Cl_2O$
Hydroquinone	9.44	$C_6H_6O_2$
1,4-Dihydroxy-2-chlorobenzene	10.60	$C_6H_5ClO_2$
1,4-Dihydroxy-2-chlorobenzene	11.20	$C_6H_5ClO_2$
2,5-Dihydroxybenzoic acid	14.02	$C_7H_6O_4$
Tetradecanoic acid	14.65	$C_{14}H_{28}O_2$
Hexadecanoic acid	16.60	$C_{16}H_{32}O_2$
Phthalates	20.95	$C_8H_4O_4$
2,6,10,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexaene	23.46	$C_{30}H_{50}$
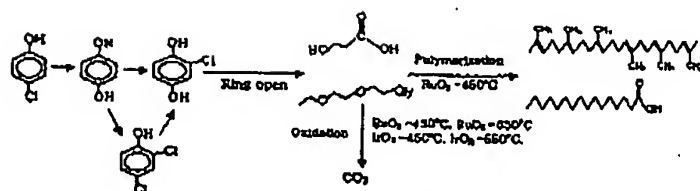
Figure 12. Plausible destruction reaction path of 4CP at Ru and Ir oxide electrodes.

1,4-dihydroxy-2-chlorobenzene, and dichlorophenols are much smaller than the other cases at 30 min of electrolysis.

It is known that the aromatic ring opens first and then conversion of the produced compounds to CO_2 follows, when phenol-like aromatic compounds are destroyed at DSA electrodes.[6,29-31] Therefore, with respect to the results of Fig. 10, Fig. 11, and the literature, plausible decomposition pathways of 4CP at Ir and Ru oxide electrodes sintered at 450-650°C can be suggested, as shown in Fig. 12. As the hydroquinone, 1,4-dihydroxy-2-chlorobenzene, and dichlorophenols increase first during the electrolysis, it is thought that 4CP is changed to hydroquinone and then the hydroquinone is converted to 1,4-dihydroxy-2-chlorobenzene, dichlorophenols, and so on. Then ring opening of the various derivatives brought about by the continuous attack of the active hydroxyl radical leads to 2-hydroxypropanoic acid and 1-(2-ethoxyethoxy)-2-hydroxyethane. Through further oxidation, the light aliphatic compounds are converted to CO_2 or synthesized to large complicated aliphatic compounds like tetradecanoic acid, hexadecanoic acid, hexamethyltetracosahexaene, etc., depending on the electrode condition. At Ir oxide electrodes sintered at 450 and 650°C and Ru oxide electrode sintered at 650°C, the combustion reaction of 4CP to CO_2 mainly occurs, and at the Ru oxide electrode sintered at 450°C, the combustion reaction and polymerization reactions of generated intermediates occur simultaneously.

From all the results, it is considered that the kind of catalytic oxide and its sintering temperature strongly affect properties of the electrode surface, which causes changes of the organic decomposition pathway as well as material and electrochemical properties. Therefore, when an oxide electrode is developed, it is considered that the electrode should be tested and evaluated in various aspects, not in one or two views.

Conclusions

Ir and Ru oxide electrodes sintered at around 650°C rather than in the range 400-550°C suggested in the literature have the highest destruction yield of 4CP. The sintering time at a high temperature above 600°C affects the oxide weight of the electrode and the electrode surface properties. With an increase of the sintering temperature, the lifetime of Ru oxide electrodes decreases, but that of Ir

oxide electrodes increases. The high temperature-sintered oxide electrode has an electrode surface structure showing an organic decomposition path different from a low temperature sintered oxide electrode. A catalytic oxide electrode for the purpose of organic destruction needs an integrated evaluation of the electrode properties in various aspects.

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